Energetic Nanocomposites with Sol-gel Chemistry: Synthesis, Safety, and Characterization

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ABSTRACT

The preparation and characterization of energetic composite materials containing nanometer-sized constituents is currently a very active and exciting area of research at laboratories around the world. Some of these efforts have produced materials that have shown very unique and important properties relative to traditional energetic materials. We have previously reported on the use of sol-gel chemical methods to prepare energetic nanocomposites. Primarily we reported on the sol-gel method to synthesize nanometer-sized ferric oxide that was combined with aluminum fuel to make pyrotechnic nanocomposites. Since then we have developed a synthetic approach that allows for the preparation of hybrid inorganic/organic energetic nanocomposites. This material has been characterized by thermal methods, energy-filtered transmission electron microscopy (EFTEM), N_2 adsoprtion/desorption methods, and Fourier-Transform (FT-IR) spectroscopy, results of which will be discussed. According to these characterization methods the organic polymer phase fills the nanopores of the composite material, providing superb mixing of the component phases in the energetic nanocomposite. The EFTEM results provide a convenient and effective way to evaluate the intimacy of mixing between these component phases. The safe handling and preparation of energetic nanocomposites is of paramount importance to this research and we will report on studies performed to ensure such.

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Introduction

As the field of nanoscience grows so does the continued demonstration of the preparation, characterization, and utility of hybrid organic/inorganic nanocomposite materials (*1-3*). Nanocomposites can be described as being composed of a host matrix phase, in which, a second distinct guest phase that has dimensions of less than 1000nm (*4*). *Energetic nanocomposites* are a class of material that have both a fuel and oxidizer component intimately mixed and where at least one of the component phases meets the size definition. A sol-gel derived pyrotechnic is an example of an energetic nanocomposite, in which metal-oxide nanoparticles react with metals and or other fuels in very exothermic reactions. The fuel resides within the pores of the solid matrix while the oxidizer comprises all of, or at least a portion, of the skeletal matrix.

The sol-gel methodology has proven to be a useful approach to the engineering and preparation of such hybrid materials and there are many examples of its successful implementation in this area (*3-5*). Sol-gel methods are frequently utilized to synthesize inorganic/organic hybrid nanocomposites, as the technique is applicable to a wide variety of materials and can be performed under ambient conditions. A hybrid material can be loosely defined as a composite of organic species (either polymeric or molecular in nature) and inorganic species that are intimately connected with one another through chemical bonding (e.g., electrostatics, hydrogen bonding, covalent bonding) or physical entwinement (*5*). Such materials often posses very unique and fascinating physical and chemical properties and are applicable to many technological fields (e.g., sensors, ceramics, thin films, optics) (*2,5*). It is certain that hybrids will have applications in the area of energetic materials.

Potential benefits of hybrids to energetic materials include, but are not limited to, enhanced mechanical properties (e.g., ease of pellet pressing, robust energetic thin films), more profound mixing of oxidizer and fuel components to augment reactivity and power output, and energetic materials with new and useful characteristics for specialty or designer applications (*6-9*). We have been actively investigating the application of sol-gel methods to the synthesis and formulation of energetic nanocomposites for the past three years (*10-12*). Here we report the preparation and characterization of a new hybrid organic/inorganic energetic nanocomposite, with a microstructure like that shown in Figure 1. The material consists of a sol-gel derived Fe_2O_3 phase thoroughly mixed with nanometer-sized ultra fine grain

inorganic sol-gel   **interpenetrating**
polymer phase   **organic polymer phase**

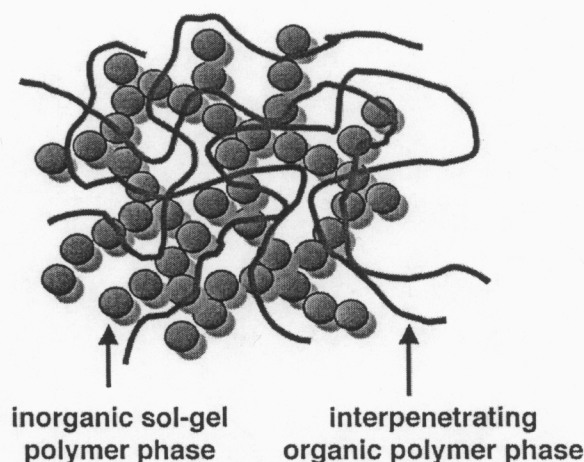**Figure 1.** *Schematic representation of the microstructure of a sol-gel derived Fe_2O_3/Viton hybrid material.*

(UFG) Al and molecularly entwined with Viton A fluoroelastomer. This unique energetic material can only be formulated using sol-gel techniques. This material can be processed into a variety of forms. Fine powders, pressed pellets, freestanding cast monoliths, and thin films of this energetic material have been

prepared using the sol-gel methodology. One potential use of this hybrid is as a high-temperature stable gas-generating material.

Experimental

Preparation of sol-gel Fe₂O₃/Al/Viton A hybrid organic/inorganic energetic nanocomposites. Ferric chloride hexahydrate, $FeCl_3 \cdot 6H_2O$ (98%), and acetone were obtained from Aldrich Chemical Co. and used as received. Absolute (200 proof) ethanol from Aaper was used as received. Viton fluoroelastomer was acquired from E.I. duPont de Nemours Chemical Co. The ultra fine grain aluminum (UFG Al) used in this study was provided by the Indian Head Division of the Naval Surface Warfare Center and was prepared via dynamic vapor phase condensation. Transmission electron microscopy analysis indicated that the UFG had a large distribution of particle sizes from ~10 to ~100 nm in diameter. The aluminum content of this material was ~70% by weight as determined by thermal gravimetric analysis.

In a typical experiment, 1.34 g of $FeCl_3 \cdot 6H_2O$ (5.0 mmol) was dissolved in 16 g of a mixed solvent (70% ethanol/30% acetone by weight) to give a clear red-orange solution that remained unchanged upon storage, under room conditions, for several months. If instead, a 4.8 g portion of propylene oxide was added to the solution it turned dark red-brown color (it has been our experience that a variety of different 1,2- and 1,3-epoxides are suitable for this step of the synthesis). (**CAUTION:** the color change is accompanied by significant heat generation, which in some cases led to rapid boil over of the synthesis solution.) To prevent a flash boil the 4.8 g of propylene oxide was added in four separate 1.2 g amounts over the period of about one hour.

A Viton A-containing solution was prepared by dissolving 5 g of Viton A fluoroelastomer in 85g of acetone (although acetone is used in this description, Viton is soluble in a variety of low molecular weight esters and ketones, which are also suitable solvents for this synthesis). After the Viton A had completely dissolved 50g of ethanol was added to the solution. Four grams of this solution was added to the propylene oxide containing Fe (III) solution from the previous paragraph. Then 0.48 g of UFG Al was added to this solution while stirring with a magnetic stir bar. The resulting mixture was stirred until the gelation occurred. Typical gel times were between 15-240 minutes.

Some nanocomposites were also made without Al. Some were also prepared using conventional μm-sized Al. Clearly other oxophillic fuel metal powders (e.g., boron, magnesium, zirconium etc.) could be used in this process. In addition this method is versatile enough that it could be extended to other sol-gel oxide systems (e.g., MoO_3, NiO, CoO, WO_3, WO_2, MoO_2, MnO_2, CuO, V_2O_5, Ta_2O_5). Finally, this is a general method for the incorporation of polymers into inorganic matrices with the only requirement being the solubility of the polymer in a chosen solvent. Thus, the general application of this method to a multitude of other polymers or organic molecules is clearly possible.

Processing Fe₂O₃/Al/Viton A and Fe₂O₃/Viton A nanocomposites. Aerogel samples were processed in Polaron^{TM} supercritical point drier. The solvent liquid in the wet gel pores was exchanged

for $CO_2(l)$ for 3-4 days, after which the temperature of the vessel was ramped up to ~45°C, while maintaining a pressure of ~100 bars. The vessel was then depressurized at a rate of about 7 bars per hour. For aerogel processing we preferred to use polyethylene vials to hold the gels during the extraction process. This was done because much less monolith cracking was observed than when Fe_2O_3 gels were processed in glass vials. Drying in a fume hood at room temperature for 14-30 days processed Xerogel samples. Under these conditions high vapor pressure solvents, like ethanol, were evaporated and the wet gels were converted to xerogels. Drying at elevated temperatures under flowing N2 atmosphere also produced Xerogels. Inert atmospheric drying of xerogels was done under ambient and elevated (~100°C) conditions. (**CAUTION**: In our hands, the wet pyrotechnic nanocomposites cannot be ignited until the drying process is complete. However, once dry, the materials will burn rapidly and vigorously if exposed to extreme thermal conditions. In addition, the autoignition of energetic nanocomposites has been observed upon rapid exposure of hot ~100°C material to ambient atmosphere.)

Physical characterization of Fe_2O_3/Al/Viton A and Fe_2O_3/Viton A nanocomposites. Fourier transform-infrared (FTIR) spectra were collected on pressed pellets containing KBr (IR-grade) and a small amount of solid sample. The spectra were collected with a Polaris™ FTIR spectrometer. Surface area determination and pore volume and size analysis was performed by BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods using an ASAP 2000 Surface area Analyzer (Micromeritics Instrument Corporation). Samples of approximately 0.1 – 0.2g were heated to 200° C under vacuum (10^{-5} Torr) for at least 24 hours to remove all adsorbed species. Nitrogen adsorption data was taken at five relative pressures from 0.05 to 0.20 at 77K, to calculate the surface area by BET theory. Bulk densities of both xerogels and aerogels were determined by measuring the dimensions and mass of each monolithic sample.

High resolution transmission electron microscopy (HRTEM) of dry Fe_2O_3 gels was performed on a Philips CM300FEG operating at 300Kev using zero loss energy filtering with a Gatan energy Imaging Filter (GIF) to remove inelastic scattering. The images where taken under BF (bright field) conditions and slightly defocused to increase contrast. The images were also recorded on a 2K x 2K CCD camera attached to the GIF. Differential thermal analysis (DTA) was performed on energetic nanocomposites that were contained in an open platinum pan. Samples were heated under both room and inert (nitrogen) atmospheres from room temperature to 1250°C at a heating rate of 20°C/min. Powder X-ray diffraction (PXRD) experiments were performed on samples powders mounted on quartz slides and loaded into a CPS120 Curved Position Sensitive Detector unit that utilizes CuK_α radiation.

Small-scale safety testing. The standard energetic material safety characterization techniques including the drop hammer, spark, and friction tests were performed on these materials. Using a type 12 drop hammer apparatus, 2.5 kg weight is dropped from a preset height onto a 35 mg pressed pellet of the material. A threshold acoustical response from diagnostic equipment determines if an explosive event occurred. Friction tests were performed by striking a ceramic stub across a portion of the material that was

spread on a ceramic stage. The stub was attached to a 36 kg weight. Spark testing was performed on small amounts of the materials using an apparatus that delivered a spark with a maximum of 1 J of energy with 510-ohm resistance. The purpose of the spark test is to exceed the maximum static energy that could be generated by a person under ideal conditions (approximately 0.1 J). With all of the safety tests at least ten replicates were performed

RESULTS AND DISCUSSION

Synthesis of organic/inorganic hybrid energetic material nanocomposites. We have reported previously on the formulation of Fe_2O_3/Al energetic nanocomposites via the *insitu* sol-gel synthesis of Fe_2O_3 in a suspension of Al nanoparticles *(10-12)*. In this case the sol-gel Fe_2O_3 phase grows around and encapsulates the solid Al particles to form an energetic nanocomposite like that shown in Figure 1. With the inorganic/organic hybrid nanocomposite described here one more component has been added: Viton A fluoroelastomer.

Viton is a highly fluorinated polymer made commercially by du Pont. It is also known as vinylidine fluoride-hexafluoropropylene copolymer and is commonly used in energetic materials formulation. Viton has several useful properties that make it an attractive component of energetic materials. Viton has excellent heat and chemical resistance as well as possessing lubricant properties in processes such as pressing or extruding. It is also highly fluorinated (60-69% F by mass), which makes it a strong oxidizer under high temperature and pressure conditions. At high temperatures the fluoroelastomer decomposes to gaseous byproducts. Finally, it is one of the few highly fluorinated polymers that has significant solubility in common organic solvents. Viton is soluble in several low molecular weight ketones, esters, and ethers. This last property makes the use of Viton in sol-gel derived hybrid materials possible.

Previous work had focused on defining the parameters of the sol-gel synthesis of nanometer-sized Fe_2O_3 from simple inexpensive Fe (III) inorganic salts, using the epoxide addition method developed at LLNL *(13-15)*. One parameter that was examined was the different types of solvents in which the synthesis was compatible. Results from this previous work were useful in determining that a common solvent system could be used as both a solvent for Viton and a medium for the sol-gel Fe_2O_3 synthesis. One solvent system that works very well is a co-solvent that is 70% ethanol and 30% acetone by weight.

In this co-solvent system sol-gel Fe_2O_3 can be made while keeping the Viton dissolved. After formation of the porous Fe_2O_3 gel network slow evaporation of the solvent leads to precipitation of the Viton polymer throughout the interconnected cavities of the material to, in effect, entwine the organic polymer in the inorganic glass. This structure is an interpenetrating network of both the organic and inorganic components, like that shown in Figure 1. The degree of mixing and contact between the two phases is superb. Any type of mechanical mixing of the two preformed components could not prepare this type of material. Physical characterization of the hybrid Fe_2O_3/Viton material supports the proposed degree of mixing of the phases.

Figure 2 contains the Fourier Transform infra-red (FT-IR) spectra of Viton A and a sol-gel Fe_2O_3/Viton A xerogel nanocomposite. There are clear strong vibrational bands
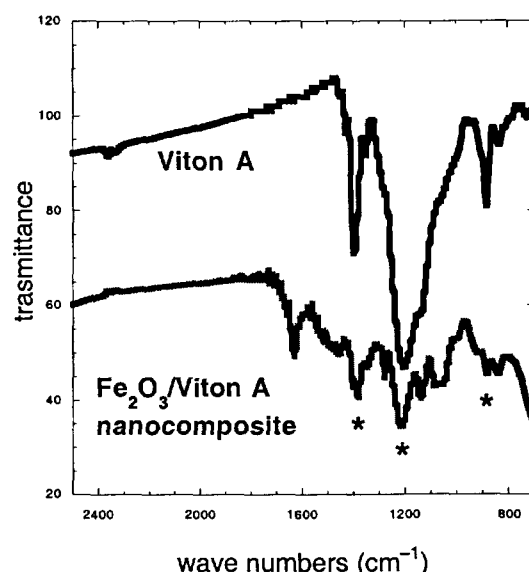

Figure 2. FT-IR spectra of Viton fluoroelastomer and a sol-gel Fe_2O_3/Viton nanocomposite.

at 883 cm^{-1}, 1205 cm^{-1}, and 1398 cm^{-1} in the spectra of both materials (note asterisks in Figure 2). This is plain evidence that the synthetic process described above has resulted in a sol-gel Fe_2O_3 material that contains Viton. Even though the FT-IR evidence indicates the presence of Viton in the composite material it provides no information as to the distribution and degree of mixing of the fluoroelastomer in the glassy inorganic matrix. For that information the pore volume and surface area of the inorganic/organic nanocomposites were measured.

Nitrogen adsorption/desorption experiments were performed on sol-gel Fe_2O_3/Viton xerogel and aerogel composites that were 80% Fe_2O_3/ 20% Viton and 100% Fe_2O_3/ 0% Viton by weight. The surface area, pore volume, and average pore size for the three materials are shown in Table 1. The nitrogen

Table 1. Summary of N_2 adsorption/desorption data for sol-gel Fe_2O_3/Viton hybrid materials.

Material	B.E.T. Surface Area (m²/g)	B.H.J. Pore Volume (cm³/g)
Fe_2O_3 xerogel	453	0.25
Fe_2O_3/Viton xerogel	6.5	<0.005
Fe_2O_3 aerogel	506	3.55
Fe_2O_3/Viton aerogel	219	1.66

adsorption data in Table 1 indicate that the Viton-containing samples have significantly smaller surface areas and pore volumes than control samples with no polymer present. This is most obvious in the xerogel sample and occurs to a smaller extent in the more open network (e.g., larger pore sizes and volume) aerogel material. This observation is consistent with our contention, that the Viton in the dried samples has effectively filled in the pores of the Fe_2O_3 sol-gel nanostructure, as is shown in Figure 1. Further interpretation of this data suggests that the Viton is very well distributed throughout the nanostructure. If instead, the Viton were present in large (μm-sized) localized domains there would logically be significant areas consisting of the highly porous sol-gel Fe_2O_3, and one would expect both the surface area and pore volumes to be much higher, especially for the xerogel sample. The extremely uniform and fine entrainment of Viton into the porous Fe_2O_3 network results in a true nanocomposite. That is, the size of the components and the dimensions of contact between those phases are in the tens of nanometers range (i.e., on the order of the size of the pore diameters (15-40 nm). With the addition of a fine fuel metal, such as UFG Al, one would expect an energetic material with interesting and potentially unique properties.

We have utilized energy filtered transmission electron microscopy (EFTEM) at LLNL to more fully elucidate the close contact between Viton and Fe_2O_3 in this material. EFTEM can be used to construct an elemental specific map of a given image. The EFTEM technique is performed using a conventional TEM microscopy in conjunction with very precise magnetic filters (*16*). Use of the magnetic image filtering system allows the construction of an image from inelastically scattered beam electrons of a given energy. The energy of the inelastically scattered electrons is related to the identity of the elements that it interacts with. By only allowing scattered electrons, of a given energy, through the filter, elemental specific maps of an image can be identified. Figure 3a contains a TEM image of a Fe_2O_3/Viton A xerogel and Figures 3b and 3c show the EFTEM maps for fluorine and Fe respectively.
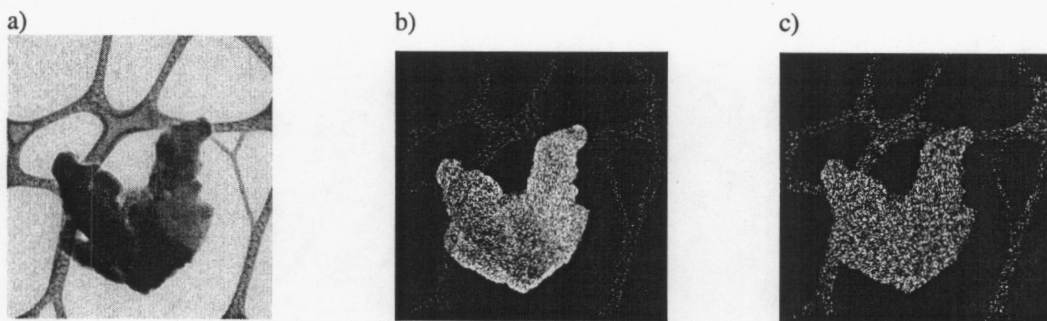

Figure 3. a) Transmission electron micrograph of sol-gel Fe_2O_3/Viton xerogel on a carbon grid. The particle is ~ 600 nm in diameter. b) Energy filtered transmission electron micrograph (EFTEM) map for Fe in the sample. c) EFTEM map for fluorine

From these images it is evident that fluorine, from the Viton, and iron, from the Fe_2O_3 xerogels are uniformly present throughout the sample. The EFTEM results indicate that F-containing Viton to be present throughout the sample indicating superb mixing of both the inorganic and organic phases, likely similar to that shown in Figure 1. Again, if the Viton were present in larger localized domains the fluorine EFTEM image would not indicate such uniform dispersion.

One of the integral features of the sol-gel method is its ability to produce materials with special shapes such as monoliths, fibers, films, and powders of uniform and very small particle sizes. We have successfully produced very fine powders of the hybrid sol-gel Fe_2O_3/UFG Al/Viton xerogel composite. There is also the potential of ambient temperature or supercritical drying to produce free-standing dry energetic composites pellets from their wet gels, without any pressing. We have demonstrated this possibility with Fe_2O_3/UFG Al aerogel composites like that shown in Figure 4.
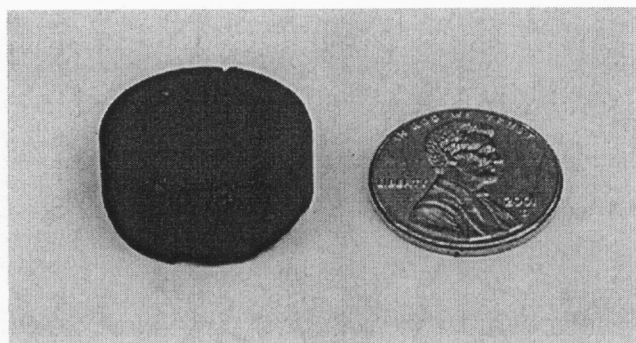

Figure 4. Photo of a freestanding cast Fe_2O_3/UFG Al aerogel nanocomposite monolith.

The importance of this particular aspect of our account cannot be overstated. It potentially allows the synthesis and shape casting of low-density energetic materials compositions, to make monolithic materials in a variety of shapes and sizes. This might eliminate the need for time-consuming, expensive, and potentially dangerous pressing and machining of the solids to make energetic materials with precise sizes, densities, and geometries.

Pressing of nanocomposite powders into dense monoliths is an important process for the potential use of such materials applications where higher energy density is required. An energetic nanocomposite powder consisting of (all values are weight percentages) 40% sol-gel Fe_2O_3, 38 % UFG Al, 11% Viton A, and 11% organic oligomers was prepared as described in the Experimental. The organic component of the materials is the byproduct of the sol-gel synthesis method. A portion of this powder was pressed using a remote apparatus, at a temperature of 80°C, to a pressure of 30,000 psi, with a dwell time of 3 minutes. The resulting right circular cylinder part is shown below in Figure 5. The measured density
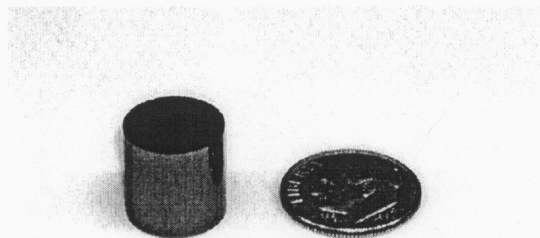
Figure 5. Photo of pressed part of sol-gel Fe_2O_3 /UFG Al/Viton A nanocomposite. Density of this part is 1.93 g/cc (~75% TMD).

of the pressed part is 1.93 g/cc. This value is between 74-77% of theoretical maximum density (TMD) for the material which is 2.5–2.6 g/cc.

The sol-gel process is very amenable to dip-, spin-, and spray-coating technologies to coat surfaces. We have utilized this property to dip-coat various substrates to make sol-gel Fe_2O_3/Al/Viton coatings. The energetic coating dries to give a nice adherent film. Preliminary experiments indicate that films of the hybrid material are self-propagating when ignited by thermal stimulus.

Some of the thermal properties of the sol-gel Fe_2O_3/UFG Al/Viton nanocomposite have been investigated. Figure 6 contains the differential thermal analysis (DTA) trace
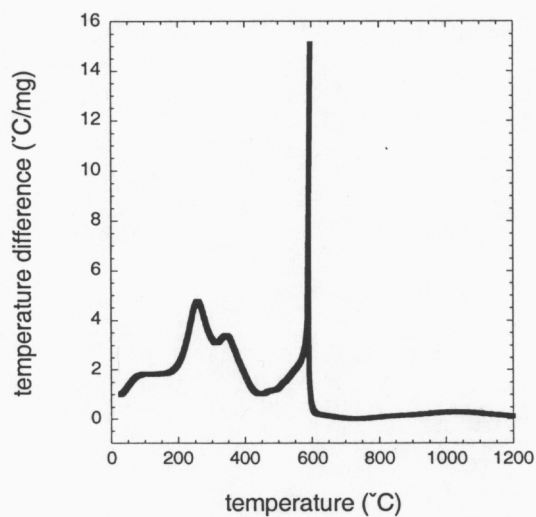
Figure 6. Differential thermal analysis trace of sol-gel Fe_2O_3/UFG Al/Viton nanocomposite performed in room air atmosphere with a heating rate of 20°C/minute.

of this material in ambient air. The sol-gel nanocomposite DTA has thermal events at ~260, ~290, and ~590°C. We have determined that the two lower temperature events are related to a phase transition and crystallization of the amorphous Fe_2O_3 phase. The exotherm at ~590°C is the most interesting as it corresponds to the thermite reaction (confirmed by powder X-ray diffraction of reaction products). This exotherm is very narrow and sharp, possibly indicating a very rapid reaction. One intriguing point to be made here is that the thermite reaction takes place at a temperature markedly below the melt phase of bulk Al ($T_m = 660°C$). This is very significant as in conventional thermite mixtures it is commonly thought that thermite reactions are initiated by the melting or decomposition of one of the constituent phases (*17-18*).

Phenomenological burn observations indicate that the material burns very rapidly and violently, essentially to completion, with the generation of significant amounts of gas. This reaction is very exothermic and results in the production of very high temperatures, intense light, and pressure from the generation of the gaseous byproducts of Viton decomposition. Future work will focus on characterization of the products and measurement of pressure generated by such composites. The burn behavior of the material qualitatively, appears to rely heavily on how dry the composite is. Figure 7 is a still image of the ignition of one such nanocomposite.

Figure 7. Still image of the thermal ignition of a 40 mg sample of sol-gel Fe_2O_3/UFG Al/Viton energetic nanocomposite.

The safe preparation and handling of energetic nanocomposites is of overriding importance to this research and we have performed small-scale safety testing on this material and the results are presented in Table 2. These results indicate that under ambient conditions the hybrid inorganic/organic energetic

Table 2. Summary of small-scale safety testing results on

Material	DH$_{50}$ (cm)	Spark	B.A.M. Friction
Fe$_2$O$_3$/UFG Al/Viton xerogel	101	0/10 @ 1J	1/10 @ 36 kg

composite is very stable to impact, is spark insensitive, and only very slightly friction sensitive.

As was mentioned in the Experimental section of this report, in our hands wet hybrid nanocomposites are safe to handle and difficult to thermal ignite. However, once dry the material burns very vigorously and rapidly with the evolution of significant amounts of gaseous species. We have observed the autoignition of the sol-gel Fe$_2$O$_3$/UFG Al/Viton nanocomposite under certain conditions. An example of an observed autoignition event is given below.

A nanocomposite of sol-gel derived Fe$_2$O$_3$/UFG Al/Viton A, had been prepared. The sample was air dried for one day under room atmosphere in a fume hood and then transferred to an oven where it was dried at 95 °C for 3 days and at 103 °C for 3 days under flowing nitrogen. The sample was removed from the oven, while still at elevated temperature, and after a 25-40 second delay it autoignited in the room air. We have observed this behavior with sample sizes as small as 2 grams. At this time it does not appear to occur with sample sizes smaller than the 2 g amount..

The reason(s) for the autoignition is not known at this time. The thermal analyses of the composite showed no major thermal events until ~600 °C (Figure 6) and thermal analyses of the pure UFG Al in air showed no thermal event until ~580 °C. To this point we have only observed this behavior in composites that contain UFG Al. Strong efforts have been and will continue to be focused on determining the cause of this event.

SUMMARY

Here we have reported the synthesis of a new inorganic/organic energetic nanocomposite using the sol-gel methodology. Careful analysis reveals the material to consist of interpenetrating inorganic sol-gel Fe$_2$O$_3$ and organic Viton networks with well dispersed UFG Al embedded in it. The material is energetic and burns very vigorously with gas evolution when thermally ignited. Under ambient conditions it has very favorable small-scale safety characteristics. Nonetheless, we have observed that rapid exposure of portion of sol-gel Fe$_2$O$_3$/UFG Al/Viton nanocomposite from a hot (~100°C) inert environment to ambient atmosphere can in some cases, result in autoignition of the material. At this time, the reasons for this behavior have not been fully resolved. We want to make it clear to persons interested in preparation and use of these materials to exercise caution. That being said, the processing options for sol-gel derived energetic materials are very versatile. We have prepared fine powders, pressed pellets, cast monoliths, and thin films of the hybrid inorganic/organic energetic nanocomposite.

Acknowledgements

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